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Spectroscopic characterization and antibacterial activities of Mn(III) complexes containing the tetradentate aza Schiff base ligands

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Abstract: The synthesis, structure, physico-chemical investigation and biological studies of some manganese (III) complexes of tetraaza Schiff base macrocycles are described. The ligands were obtained by condensation of *ortho*-phthalaldehyde with different diamines in methonal. The metal complexes of Mn (III) were synthesized and isolated as solid products and characterized by analytical means as well as by spectral techniques such as FT-IR, Mass and UV-Vis spectrometry. On the basis of these studies, a five coordinate square pyramidal geometry for all of these complexes have been proposed. These complexes were also tested for their *in vitro* antimicrobial activities against some bacterial strains to assess their inhibiting potential and the activities shown by these complexes were compared with standard drugs.
Key words: Mn(III) complexes, Macrocyclic Schiff bases, Spectroscopic characterization, Antibacterial studies.

1. Introduction

Over couple years of extensive research work in many laboratories worldwide, macrocyclic chemistry is a well-established and highly recognized branch of science[1,2]. Schiff bases have therefore provided a foundation stone for the building of contemporary macrocyclic chemistry[2]. A wide range of Schiff base macrocycles has evolved from the early studies[3-10]. The role of the metal ion in these metal-ion ternplated cyclisations is to control the supramolecular assembly of pre-cyclisation fragments, most likely through the formation of metal complexes derived from the precursors. The desired cyclisation product then results from an intramolecular interaction in the transition state. Notably, Metal-Schiff-base complexes are excellent coordination/organometallic compounds to construct supramolecular compounds due to their powerful applications in the field of catalysis, magnetic materials, and bioinorganic chemistry[3-11].

The macrocyclic Schiff base obtained has been versatile in forming a series of complexes with Cr(III)[12,13], Mn(II)[13], Mn(III)[14], Fe(II)[15], Fe(III)[13],Co(II)[4,15,16], Ni(II)[6,16], Cu(II)[3,15,16], Zn(II)[15,16], Ru(II)[9,10], Ru(III)[13], Rh(III)[5], Ir(III)[13], Pd(II)[8] and Pt(II)[13] ions under well defined conditions and these complexes have been investigated with particular reference to the structural aspects of the ligand moiety in the metal complexes. The coordination chemistry of macrocyclic ligands is a fascinating area of intense study for inorganic chemists[2,17-19]. The aspect of interest in macrocyclic ligands is raised from features such as the nature, number and arrangement of ligand donors, as well as ligand conjugation, substitution and flexibility, which produce different types of macrocyclic molecules suitable for specific uses[2]. Transition metal complexes of tetradentate Schiff base ligands find applications in catalysis[5,6,10] and as biomimetic enzyme models[20]. Although a large number of compounds of the type $M(N_2O_2)$[3-6,9,21],

$M(N_2S_2)$[22] and $M(N_4)$[3-6,9] (using the binding atom representation), have been synthesized and characterized, there are scarce reports on the N_4 tetradentate Schiff base complexes of Manganese (III)[14,23]. Furthermore, orthophthalaldehyde (OPA) based macrocyclic metal compounds were synthesized by template method involving the direct treatment of OPA with diamine in the presence of metal salts[24-26] . However, based on the literature survey there are no reports on the synthesis of macrocyclic Mn(III) compounds derived from o-phthalaldehyde. Thus, the aim of the present work is to synthesize and characterize complexes of Manganese (III) with potential biologically active macrocyclic Schiff base ligand and to determine their antimicrobial activities.

2. Experimental

2.1. Materials and Methods

Solvents were dried and purified before being used. Other reagents were purchased from Merck or Fluka and were used without further purification. Six macrocyclic ligands viz. 7,8,9,18,19,20-hexahydrodibenzo[*g,p*][1,2,4,5,10,11,13,14]-octaazacyclooctadecine-8,19-dione [HBOADO], 7,8,17,18-tetrahydrodibenzo[*f,n*] [1,2,4,9,11,12]-hexaazacyclohexadecine-8, 17-dione [TBACD],3,4,5,6,7,8,9,10-octahydro-2,5,8,11-benzotetra azacyclotetradecine [OBACD], 7,8,9,18,19,20-hexahydrodibenzo[*g,p*] [1,2,4,5,10,11,13,14]-octaazacyclooctadecine-8,19-dithione [HBOADT], 7,16-dihydrodibenzo[*e,l*] [1,3,8,10] tetraazacyclo tetradecine-7,16-dithione[DBACDT] and 7,8,17,18-tetrahydrodibenzo[*f,n*] [1,2,4,9,11,12]hexa azacyclohexadecine-8,17-dithione [TBAHD] were newly prepared and characterized. Organisms like Bacillus subtilis (MTCC–619), Staphylococcus aureus (MTCC–96), Escherichia coli (MTCC–722) and Klebsiella pneumonia (MTCC–109) from IMTECH, Chandigarh were used for antimicrobial studies.

2.2. Physical Measurements

CHN analyses were carried out using a Perkin Elmer 2400 elemental analyze. The UV–Vis measurements were carried out in DMF solution using a Shimadzu UV-160A, a UV-Visible double beam spectrophotometer equipped with matched quartz cells of path length 1 cm. Infrared spectra were obtained on a Perkin-Elmer 283 IR spectrophotometer as KBr/CsBr pellets. Mass spectrum was recorded on a Finnigan mass spectrometer. Conductance measurements were performed using a Digisun Digital conductivity meter model DL-909. Gouy balance calibrated with $Hg[Co(NCS)_4]$ was used for the determination of magnetic susceptibilities of complexes in solid state at room temperature. The melting points of all the macrocyclic ligands and macrocyclic metal compounds were obtained on a Buchi- 510 melting point apparatus.

2.3. Synthesis of macrocyclic Mn(III) complexes

The metal complexes were prepared by the following general procedure. To a hot magnetically stirred methanolic solution (50 mL) of the macrcyclic ligand, added aqueous/methanolic solution of manganese (III) chloride salts in equimolar ratios. The solution was refluxed on a water-bath for 3-4 h. Then the volume of the solution was reduced to half the initial volume by evaporating on a water-bath. On cooling, the complex separated was filtered, dried and further purified by recrystallization from hot methanol solution and dried in a vacuum desiccator over P_4O_{10}.

3. Results and Discussion

In the present investigations, six new macrocyclic Mn(III) complexes were synthesized by treating manganese chloride with six N_4 donor macrocyclic ligands separately. The percentages of carbon, hydrogen and nitrogen were determined experimentally using CHN analyzer. The percentage of maganese in macrocyclic Mn(III) complexes were determined by using gravimetric procedure. The tests for anions are positive before decomposing and after decomposing the chelates with concentrated HNO3 showing their presence outside as well as inside of coordination sphere. Several attempts failed to obtain a single crystal suitable for X-ray crystallography. However, the analytical, spectroscopic and magnetic data enable us to predict the possible structure of the synthesized complexes. The physical and analytical data (**Table-1**) for the newly synthesized macrocyclic Mn(III) complexes is in good agreement with the proposed molecular formulae viz. $[Mn(L)Cl]Cl_2$ (Where L= tetraaza macrocyclic ligand).

3.1. Infrared spectral data

In the IR spectra of macrocyclic Mn(III) complexes, a medium intensity band due to $\upsilon_{C=N}$ was shifted towards lower side about 25-35 cm^{-1} compared to ligand spectra and appeared in the range of 1625-1600 cm^{-1}. This supports the fact that the ligands coordinate to the metal ions through the nitrogen of C=N group in all the complexes[8,9]. This fact is further supported by the appearance of a band in the region of 530-500 cm^{-1} assignable to υ_{M-N} vibration[11,27-31]. However, in the complex-**3** υ_{NH} band was observed at 3320 cm^{-1}. This band was shifted towards lower side about 35 cm^{-1} compared to the ligand spectrum indicates the coordination to the metal through nitrogen of NH group[8,10]. The bands present in the range 305-325 cm^{-1} may be assigned due to ν(M─Cl) vibration[5,6,27,32-34].The characteristic bands due to the $\upsilon_{C=O}/\upsilon_{C=S}$ in the spectra of respective macrocyclic Mn(III) compounds were remain almost unshifted[8,10,12]. All the characteristic bands due to the aromatic rings were also present in the expected regions[5,6]in all the macrocyclic Mn(III) compounds (**Table-2**).

Table 1: Physical and analytical data of macrocyclic Mn(III) complexes.

Comp. No.	Mn(III) compound/ Molecular formula	Λ_M	Analyses (%) Found (Calculated)			
			C	H	N	Mn
1.	[Mn(HBOADO)Cl]Cl2C_{18} $H_{16}Cl_3N_8O_2Mn$	169	40.24 (40.21)	3.03 (3.00)	20.82 (20.84)	10.20 (10.22)
2.	[Mn(TBACD)Cl]Cl2 $C_{18}H_{14}Cl_3N_6O_2Mn$	160	42.60 (42.59)	2.79 (2.78)	16.54 (16.56)	10.80 (10.82)
3.	[Mn(OBACD)Cl]Cl2 $C_{14}H_{20}Cl_3N_4Mn$	165	41.50 (41.45)	5.01 (4.97)	13.79 (13.81)	13.55 (13.54)
4.	[Mn(HBOADT)Cl]Cl2C_{18} $H_{16}Cl_3N_8S_2Mn$	175	37.92 (37.94)	2.84 (2.83)	19.70 (19.67)	9.65 (9.64)
5.	[Mn(DBACDT)Cl]Cl2C_{18} $H_{12}Cl_3N_4S_2Mn$	172	42.44 (42.41)	2.38 (2.37)	10.98 (10.99)	10.79 (10.78)
6.	[Mn(TBAHD)Cl]Cl2 $C_{18}H_{14}Cl_3N_6S_2Mn$	166	40.07 (40.05)	2.60 (2.61)	15.59 (15.57)	10.17 (10.18)

Table 2 : Infrared spectral data of macrocyclic Mn(III) complexes.

Comp. No.	Mn(III) compound	Selected IR bands (cm^{-1})			
		$\upsilon_{C=N}$	υ_{NH}	υ_{Mn-N}	Anion peaks
1.	[Mn(HBOADO)Cl]Cl2	1575	3325	520	318
2.	[Mn(TBACD)Cl]Cl2	1595	3330	515	310
3.	[Mn(OBACD)Cl]Cl2	1585	3315	530	315
4.	[Mn(HBOADT)Cl]Cl2	1596	3335	500	305
5.	[Mn(DBACDT)Cl]Cl2	1588	-	518	325
6.	[Mn(TBAHD)Cl]Cl2	1580	3360	525	320

3.2. Mass spectral analysis

The FAB mass spectra of Mn(III) macrocyclic complexes have been recorded. In the mass spectra of respective macrocyclic Mn(III) compounds, molecular ion peaks, m/z (M^+) were observed at 537 for [Mn(HBOADO)Cl]Cl2, 507 for [Mn(TBACD)Cl]Cl2, 405 for [Mn(OBACD)Cl]Cl2, 569 for[Mn(HBOADT)Cl]Cl2, 509 for [Mn(DBACDT)Cl]Cl2 and 539 for [Mn(TBAHD)Cl]Cl2. The proposed molecular formula of theses complexes were confirmed by comparing their molecular formula weights with m/z values. This data is in good agreement with the respective molecular formulae.

3.3. Electronic spectral analysis

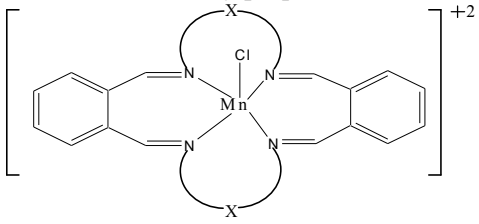
The electronic spectra of manganese complex show three d-d bands which lay in the range 12310-12620, 16150- 18880 and 35350-35690 cm^{-1}. The higher energy band at 35390-35690 cm^{-1} may be assigned due to charge transfer transitions. The spectra resemble to those reported for five coordinate square pyramidal Mn(III) complexes[14,35,36]. This idea is further supported by the presence of the broad ligand field band at 20420 cm-1 diagnostic of C_{4V} symmetry, and thus the various bands may be assigned as follows: $^5B_1 \rightarrow {}^5A_1$, $^5B_1 \rightarrow {}^5B_2$, and $^5B_1 \rightarrow {}^5E$, respectively. The band assignment in single electron transition may be made as: $dz^2 \rightarrow dx^2\text{-}y^2$, $dxy \rightarrow dx^2\text{-}y^2$ and $dxz, dyz \rightarrow dx^2\text{-}y^2$, respectively in order of increasing energy. However, the complexes do not have idealized C_{4V} symmetry.

3.4. Molar conductance, magnetic susceptibility and thermal studies

The molar conductance values for all the macrocyclic Mn(III) complexes (10^{-3} M) were determined in DMSO. These values were found between 160 and 175 $ohm^{-1}cm^2mol^{-1}$ indicating 1:2 electrolytic nature[14,35]. The electrolytic nature of these compounds is due to the presence of two chloride ions outside the coordination sphere. The presence of chloride ions in these compounds was detected by the addition of silver nitrate reagent leading to the formation of white precipitate. Magnetic moments of Mn(III) complexes were found in the range of 4.85-4.92 B.M. at room

temperature which is close to the predicted values for three unpaired electrons in the metal ion[14,35]. The thermal analysis data of Mn(III) complexes indicates that they are stable up to 250°C and hence exist in anhydrous state. The DTA curves show no endothermic peaks up to 250°C confirming the absence of lattice or coordinated water molecules in the complexes [29-31]. The sharp decomposition corresponding to the loss of organic moiety in complexes can be seen in the DTA curves which contained one sharp exothermic peak falling in the range of 250-275°C. The final product of decomposition of all the complexes above 590°C corresponds to metal oxide.

On the basis of analytical and spectral data, a five coordinated square pyramidal geometry (**Scheme 1**) have been tentatively proposed for all of these complexes.



Where

HBOADO ; X= -NHCONH-
TBACD ; X= -NHCO-
HBOADT ; X= -NHCSNH-
DBACDT ; X= -CS-
TBAHD ; X= -CSNH-

Scheme 1: Representative structures of macrocyclic Mn(III) complexs

3.5. Evaluation of antimicrobial activity

Antibacterial activities of macrocyclic Mn(III) complexes were studied along with existing antibacterial drug *viz.* streptomycin. The minimum inhibitory concentration (MIC) of Mn(III) complexes against *Bacillus subtilis* (MTCC–619), *Staphylococcus aureus* (MTCC–96), *Escherichia coli* (MTCC–722) and *Klebsiella pneumonia* (MTCC–109 (bacterial strains) were determined by liquid dilution method[7,37]. Stock solutions of test samples with 2.5, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 µg/ml concentrations were prepared with appropriate solvent. The solutions of standard drug, Streptomycin were prepared in the same concentrations. Inoculums of the bacterial culture were also prepared. To a series of tubes containing 1 ml each of compound (macrocyclic Mn(III) complexes) solution with different concentrations and 0.2 ml of the inoculum was added. Further 4.0 ml of the sterile water was added to each of the test tubes. These test tubes were incubated for 24 h and observed for the presence of turbidity. This method was repeated by changing compounds with standard drug (Streptomycin) for comparison. The minimum inhibitory concentration at which no growth was observed was taken as the MIC values.

Table 3: Minimum inhibitory concentrations of the Mn(III) complexes and existing antibiotics.

S. No.	Mn(III) compound	Range of concentration (2.5-50 µg/ml)			
		MTCC-619	MTCC- 96	MTCC-722	MTCC-109
1.	[Mn(HBOADO)Cl]Cl2	15	25	30	20
2.	[Mn(TBACD)Cl]Cl2	25	30	30	25
3.	[Mn(OBACD)Cl]Cl2	30	40	35	35
4.	[Mn(HBOADT)Cl]Cl2	2.5	5.0	2.5	2.5
5.	[Mn(DBACDT)Cl]Cl2	5.0	10	15	10
6.	[Mn(TBAHD)Cl]Cl2	5.0	5.0	10	5.0
7.	Streptomycin	10	15	20	15

Comparison of MIC values (in µg/ml) of Mn(III) complexes and standard drugs against different bacteria are presented in Table 3 and Figure 1. From these results, it is evident that [Mn(HBOADT)Cl]Cl2, [Mn(DBACDT)Cl]Cl2 and [Mn(TBAHD)Cl]Cl2 complexes showing superior activity when compared to Streptomycin and towards inhibiting all tested bacterial strains. Though there is sufficient increase in the antibacterial activity of rest macrocyclic Mn(III) complexes as compared to the free ligand, it could not reach the effectiveness of the conventional standard drug Streptomycin. The results showed that the macrocyclic Mn(III) complexes are more toxic as compared with their parent ligand against the same microorganism under identical experimental conditions. The increase in the antimicrobial activity of Mn(III) chelate may be due to the effect of the metal ion on the normal cell process. A possible mode of toxicity increase may be considered in the light of Tweedy's chelation theory[38]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophillic character of the central metal atom, which subsequently favors its permeation through the lipid layers of cell membrane[9]. The general trend of growth of inhibition against the bacteria was found to lie in the order [Mn(OBACD)Cl]Cl2 < [Mn(TBACD)Cl]Cl2 < [Mn(HBOADO)Cl]Cl2 < Streptomycin < [Mn(DBACDT)Cl]Cl2 < [Mn(TBAHD)Cl]Cl2 < [Mn(HBOADT)Cl]Cl2.

4. Conclusions

By the elemental, IR, UV–Vis, mass spectra, magnetic, conductivity measurements and thermal studies indicate that the complexes are of the type $[Mn(L)Cl]Cl_2$ (Where L= tetraaza macrocyclic ligand) with a square pyramidal ligand field. Since, two chloride ions are present outside the coordination sphere, these compounds have electrolytic nature. Furthermore, these macrocyclic Mn(III) complexes were found to have significant antibacterial activity.

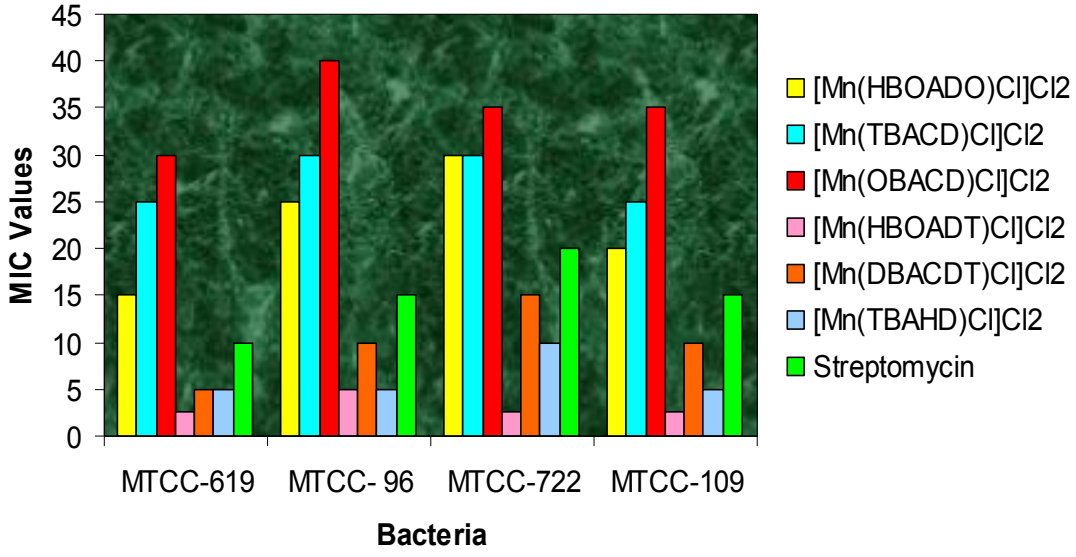


Figure 1. Comparison of MIC values (in µg/ml) of macrocyclic manganese complexes and streptomycin against different bacteria.

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